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TRANSMITTAL FORM

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First Named Inventor	Henry Alfred Craddock
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Examiner Name	Not Yet Assigned
Total Number of Pages in This Submission	
Attorney Docket Number	08830-0268 US1

ENCLOSURES *(check all that apply)*

- ☐ Fee Transmittal Form
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- ☐ Amendment / Reply
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  - ☐ Affidavits/declaration(s)
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- ☑ Certified Copy of Priority Document(s)
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Remarks

SIGNATURE OF APPLICANT, ATTORNEY, OR AGENT

Firm *or* Individual name	Daniel A. Monaco Drinker Biddle & Reath LLP
Signature	
Date	6-10-04

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Typed or printed name	Shannon R. Smith		
Signature	Shannon R. Smith	Date	6-10-04

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

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1/77

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01/7700 0.00-0305862.5

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14 MAR 2003
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The Patent Office

Cardiff Road
Newport
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NP10 8QQ

1. Your reference — P33729-/SGR/CWA

2. Patent application number *(The Patent Office will fill in this part)* — 0305862.5 — 14 MAR 2003

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

TR Oil Services Limited
Howe Moss Place
Kirkhill Industrial Estate
Dyce
Aberdeen AB2 0GL
United Kingdom

Patents ADP number *(if you know it)* 8587867001

If the applicant is a corporate body, give the country/state of its incorporation

4. Title of the invention — "Method and Chemicals"

5. Name of your agent *(if you have one)*

"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

Murgitroyd & Company
Scotland House
165-169 Scotland Street
Glasgow
G5 8PL

Patents ADP number *(if you know it)* 11980155

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

a) any applicant named in part 3 is not an inventor, or
b) there is an inventor who is not named as an applicant, or
c) any named applicant is a corporate body.
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Patent Form 1/77

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Description	15
Claim *(s)*	-
Abstract	-
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Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	-
Request for preliminary examination and search *(Patents Form 9/77)*	-
Request for substantive examination *(Patents Form 10/77)*	-
Any other documents *(please specify)*	-

11. I/We request the grant of a patent on the basis of this application.

Signature Murgitroyd & Co. Date 13/03/2003

Murgitroyd & Company

12. Name and daytime telephone number of person to contact in the United Kingdom: Craig Watson 01224 706616

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"Method and Chemicals"

This invention relates to a method and chemicals for inhibiting corrosion in an aqueous environment and particularly but not exclusively to the use of small organo-sulphur molecules such as thiohydantoins as corrosion inhibitors or corrosion inhibitor synergists in the oil industry.

Advances in drilling and completion technology have revolutionised new field development and the use of subsea wells with long tie backs is now common. The low temperatures and long fluid transport times under subsea conditions often result in a wide variety of production chemistry related problems, including corrosion, scale, wax and asphaltene deposition, hydrate formation and bacterial growth.

It is known that alkyl quaternary ammonium salts can be used as corrosion inhibitors and these are commercially available under the brand names such as Dodigen™ and Dodicon™. It is thought that the

molecules of these salts attach to the downhole metal structure - normally via a nitrogen atom present in the molecule - and through a process of self-assembly provide a physical barrier or film between water and the structure. This film prevents corrosion of the structure because the water (which includes corrosion causing agents such as CO_2 and H_2S) is prevented from contacting the structure. Also, the organic groups present in the inhibitors, being hydrophobic, repel water.

It is known that the addition of other chemicals, known as synergists, can significantly increase the effectiveness of the corrosion inhibitors. The synergists are thought to help the inhibitors bond with the metal structure to provide a more effective physical barrier to water.

The corrosion rates for some alkyl quaternary ammonium salt corrosion inhibitors used with and without synergists are shown in the table below. It is shown from these results that although the ammonium salt and the synergist reduce the corrosion rate moderately when used independently of each other, when used together their combination reduces the corrosion rate significantly.

chemical	corrosion rate
blank	32.87 mpy
5ppm thiosulphate	17.93 mpy
20ppm Dodigen 2808	17.46 mpy
20ppm Dodigen 2808+5ppm thiosulphate	0.61 mpy
20ppm Dodigen 179	27.40 mpy
20ppm Dodigen 179+5ppm thiosulphate	1.00 mpy

Thioacetamide (CH_3CSNH_2) has been identified as a persistent corrosion inhibitor/corrosion inhibitor synergist. However, it is known as a possible carcinogen and is therefore unsuitable for field deployment.

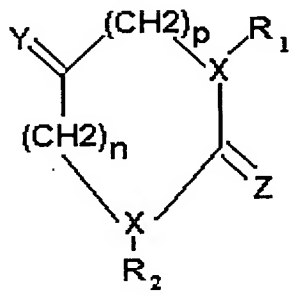
Sodium thiosulphate (STS) and thioglycolic acid (TGA) are also known corrosion inhibitors but suffer from the disadvantages that the former can promote pitting of stainless steels at high dose rates whilst the latter is a toxic and stench chemical.

Substituted thiohydantoins are used in the identification of the N-terminal amino acid units of a peptide chain by means of the Edman Degradation. A free amine function bonds to a phenyl isothiocyanate reagent and produces a thiohydantoin hetrocycle incorporating the N-terminal amino acid together with a shortened peptide chain. Characteristic hydantoin derivatives of all the amino acids have been catalogued so identification of the terminal units is accomplished by comparison.

Thiohydantoins are commercially available from Sigma-Aldridge and other chemical suppliers.

Thiohydantoin is not carcinogenic.

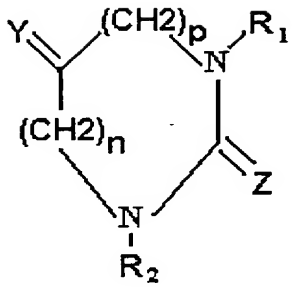
According to a first aspect of the present invention, there is provided a method of inhibiting corrosion in an aqueous environment, the method comprising the step of injecting a chemical according to the following formula into an aqueous environment:-



wherein n is any number between 1 and 100, p is any number between 0 and 100, R_1 is H or an organic group, R_2 is H or an organic group, and X, Y and Z are independently any suitable atom or functional group.

Preferably, X is a nitrogen atom or alternatively a phosphorus atom. Preferably Y is an oxygen atom or alternatively a S atom. Preferably Z is a sulphur atom or alternatively an O atom.

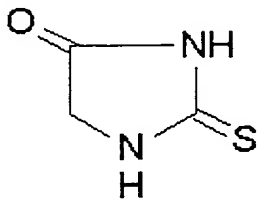
Preferably the chemical comprisies a structure according to the following formula:-



Preferably P is of the value of 0 or 1. Where P is greater than or equal to one, the C_p atom typically bonds to the C_y atom and to the X atom or functional group; there is typically no covalent bond between the C_y atom and the X atom or functional group. Where P is zero there is typically a covalent bond between the C_y atom and the X atom or functional group.

Preferably the value of n is 1 or 2, more preferably 1.

Preferably, the chemical is 2-thiohydantoin, as represented by the following formula:-



Preferably, the aqueous environment is an oilfield environment.

The aqueous environment may be any one of a cooling water system, a water flood system and a produced water system. The aqueous environment may also be in crude oil systems or gas systems and may be deployed downhole, topside, pipeline or during refining.

The aqueous environment may include CO_2, H_2S, O_2, brine, condensed water, crude oil, gas condensate, or any combination of the said or other species.

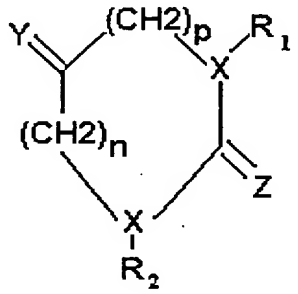
The chemical may be deployed continuously or alternatively as a batch. The chemical may be used in low or high shear conditions.

The chemical may be used as a corrosion inhibitor or as a corrosion inhibitor synergist in combination with an organic corrosion inhibitor. Examples of oilfield corrosion inhibitors for which synergists are useful include amines, amido amines, quatazamines, imidazolines, amides, ethoxylated amines, quaternary ammonium salts, betaines, phosphate esters, sulphonates, polyaspartates, as part of a combined product, i.e. corrosion inhibitor combined with scale inhibitor, wax inhibitor, hydrate inhibitor, demulsifier, deoiler or any other corrosion inhibitor. Oligomers and polymers of these corrosion inhibitors may also be used with the chemical.

When used as a synergist, R_1 and R_2 are preferably organic groups such as alkyl groups. Preferably R_1

and R_2 comprise between 1 and 40 carbon atoms, more preferably around 18 carbon atoms.

According to a second aspect of invention, there is provided a chemical for use as a corrosion inhibitor, or as a corrosion inhibitor synergist, the chemical being represented by the following formula:-

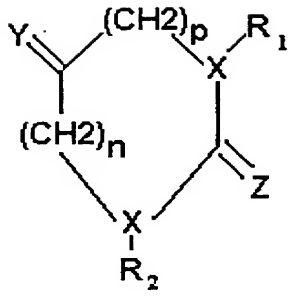


wherein n is any number between 1 and 100, p is any number between 0 and 100, R_1 is H or an organic group, R_2 is H or an organic group, and X, Y and Z are independently any suitable atom or functional group.

Preferably the chemical of the second aspect of the invention is used for the method according to the first aspect of the invention.

Preferably the chemical of the second aspect of the invention is the chemical as described with respect to the first aspect of the invention.

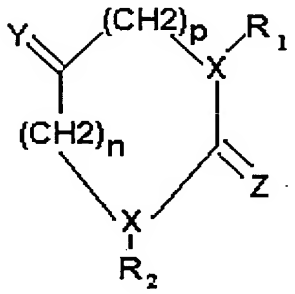
The invention also provides the use of a chemical of the following formula



wherein n is any number between 1 and 100, p is any number between 0 and 100, R_1 is H or an organic group, R_2 is H or an organic group, and X, Y and Z are independently any suitable atom or functional group;

as a corrosion inhibitor or as a corrosion inhibitor synergist.

The invention also provides a corrosion inhibitor or corrosion inhibitor synergist, comprising a chemical of the following formula



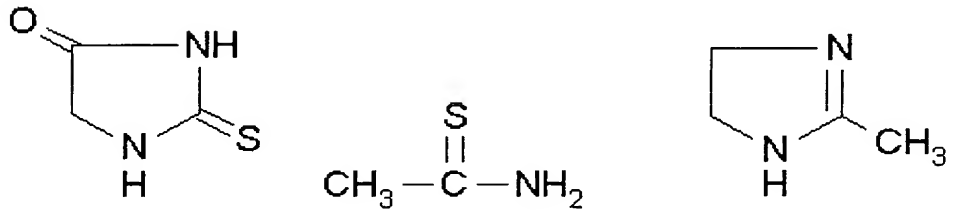
wherein n is any number between 1 and 100, p is any number between 0 and 100, R_1 is H or an organic group, R_2 is H or an organic group, and X, Y and Z

are independently any suitable atom or functional group.

Embodiments of the invention will now be described by way of example only.

In order to investigate the efficiency of corrosion inhibition by thiohydantoin, aqueous linear polarisation resistance (LPR) bubble tests were carried out and compared with thioacetamide. Thiohydantoin is not carcinogenic. As the basic structure of thiohydantoin is related to imidazoline it was also compared against 2-methyl-2 imidazoline a similar suphur free imidazoline.

The structures of 2-thiohydantoin, thioacetamide and 2-methyl-2-imidazoline are shown below:-



2-thiohydantoin thioacetamide 2-methyl-2-imidazoline

The procedure for conducting the bubble test is generally based on a protocol developed by BP Sunbury and described in "Corrosion Inhibitor Test Methods", S Webster, A J McMahon, D M E Paisley, D Harrop, BP Sunbury report ESR.94.ER.054, dated November 1996 and also "Corrosion Inhibitor Guidelines", A J McMahon, S Groves, BP Sunbury report ESR.95.ER.050, dated 1996.

The procedure also makes use of principles from the following ASTM standards,

- G1-90 (1999) "Standard Practise for Preparing, Cleaning and Evaluating Corrosion Test Specimens"

- G102-89 (1999) "Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements"

- G5-94 (1999) "Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements"

- G59-97 "Standard Practice for Conducting Potentiodynamic Polarization Resistance Measurements"

- G61-86 (1998) "Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys".

The bubble test comprises a carbon steel electrode immersed in a bath of oilfield brine and possibly a crude oil to simulate the environment in which the corrosion inhibitor would be used. A gas, commonly CO_2 which is a corrosion causing agent, is bubbled through the brine mixture and the corrosion rate of the electrode in the absence of a corrosion inhibitor is measured using the linear polarisation

resistance method (LPR) or AC Impedance (EIS). The inhibitor under examination is then added, normally after two hours, and the subsequent polarisation resistance/ corrosion rate is recorded. This data can be used to calculate the inhibitor efficiency.

Results

Aqueous bubble tests were carried out on the three inhibitors/synergists in duplicate.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
thioacetamide	1	144.96	5.58	96.15
thioacetamide	1	152.60	3.55	97.67
thiohydantoin	1	163.47	18.07	88.95
thiohydantoin	1	141.09	9.42	93.32
2-methyl-2-imidazoline	1	146.81	216.65	0
2-methyl-2-imidazoline	1	144.07	193.81	0

Table 1 : Aqueous Bubble Test Results using 3% NaCl at 50°C

In these tests the thiohydantoin did not perform as well as thioacetamide. Methyl imidazoline performed poorly as the corrosion rate actually increased, from 145mpy to 200mpy and therefore it was decided not to continue testing with this product.

The aqueous bubble tests were repeated using BP Forties synthetic brine and the results are shown in table 2. In this test the performances of

thioacetamide and thiohydantoin had improved with a dramatic improvement in the result from thiohydantoin when compared to the bubble test with 3% NaCl.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
Thioacetamide	1	146.84	1.29	99.12
Thioacetamide	1	208.29	0.82	99.61
Thiohydantoin	1	174.73	1.64	99.06
Thiohydantoin	1	132.10	1.07	99.19

Table 2 : Aqueous Bubble Test Results using Forties Synthetic Brine at 50°C

Partition bubble tests were performed on thioacetamide and thiohydantoin. In this test 600ml of brine is first added to a test cell. A mixture of a further 200 ml brine and 200 ml crude oil is made up and thoroughly mixed before being added to the brine in the test cell.

The fluids used in the partition bubble tests were Forties synthetic brine and Forties crude oil. 800ml of brine and 200ml of crude were used to investigate the partition efficiency of the inhibitors/synergists and the results are shown in table 3 below.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
Thioacetamide	1	241.36	0.97	99.60
Thioacetamide	1	211.37	0.70	99.67

Thiohydantoin	1	239.59	2.41	98.99
Thiohydantoin	1	202.79	1.35	99.33

Table 3 : Partition Bubble Test Results using Forties Synthetic Brine at 50°C

The performance of thioacetamide and thiohydantoin was similar to that achieved under aqueous Forties conditions. (Table 2)

Thiohydantoin was evaluated further as a corrosion inhibitor and as a corrosion inhibitor synergist using a rotating cylinder electrode (RCE) at 5000rpm (29.5 Pa). The rotating cylinder electrode test comprises a rotating carbon steel electrode immersed in a bath of oilfield brine and possibly crude oil to simulate the shear stresses that may be encountered in the environment which the corrosion inhibitor would be used. In certain tests, pre-partitioning of the inhibitor is carried out with brine/crude shaken with inhibitor present and the separated brine used for the tests. A gas, commonly CO_2, is bubbled through the brine mixture and the electrode rotation started at the required rate. The corrosion rate of the brine is then measured using the linear polarisation resistance method and/or AC impedance. If unpartitioned brine is used the inhibitor being tested is added at this point and the inhibitor rate measured. If partitioned brine is used the initial rate is the inhibitor corrosion rate and is compared to partitioned brine without inhibitor to calculate the inhibition ratio.

The results are shown in Table 4.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy)		% Inhibition
		Before inhib.	After inhib.	
thiohydantoin	1	160.50	4.65	97.10
thiohydantoin	1	90.01	11.24	87.51
thiohydantoin(1ppm) + QUAT(2ppm)	3	91.76	2.80	96.95
thiohydantoin(1ppm) + QUAT(2ppm)	3	90.06	5.59	93.79

Table 4 : Rotating Cylinder Electrode Test using 3%NaCl Brine at 50°C

The quantity of thiohydantoin used in the formulation with the QUAT is the same as in previous tests. The QUAT is CLARIANT™ Dodigen 2808, a coco benzyl quat.

A further RCE test was used to investigate the persistency of thiohydantoin. The brine was replaced with fresh brine after 20 hours. Although some persistency was observed the corrosion rate increased from 11mpy to 35 mpy and the results are shown in Table 5.

Inhibitor	Dose (ppm)	Corrosion Rate (mpy) % Inhibition		
		Before inhib.	After inhib.	Fresh brine
Thiohydantoin	1	90.01	11.25	35.45

Table 5 : Persistency Test using 3%NaCl Brine at 50°C

On the basis of these tests thiohydantoin is a viable and non-carcinogenic alternative to thioacetamide. Thiohydantoin matches the excellent corrosion inhibition of thioacetamide in a series of static and dynamic tests. Indeed, it is considered that thiohydantoin is suitable to be used as a corrosion inhibitor in its own right rather than simply as a synergist for known corrosion inhibitors. In such cases, the hydrogens attached to the nitrogen atoms may be replaced by organic or alkyl groups of the order of C_1-C_{40} but preferably around C_{18}.

A six membered ring equivalent such as a pyrimidine based ring is also effective against corrosion inhibition.

Thiohydantoin (and derivatives) are also effective against other known corrosion causing agents, such as H_2S.

Modifications and variations may be made without departing from the scope of the invention.